A convenient solution to the multiple parentage problem: test of a MRCC method and prospects

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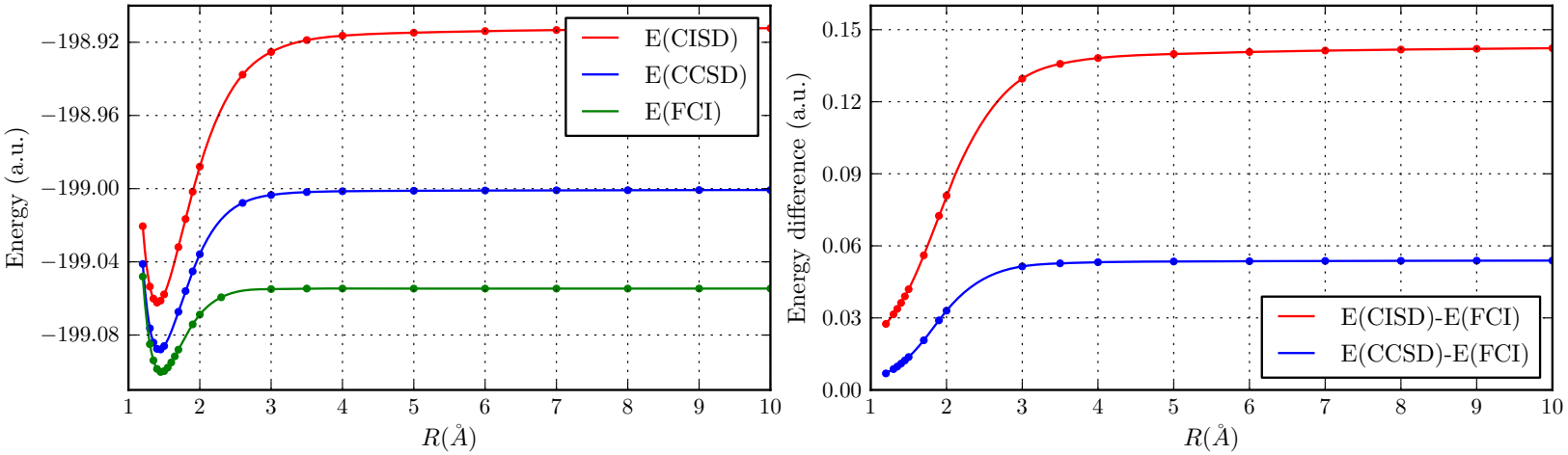
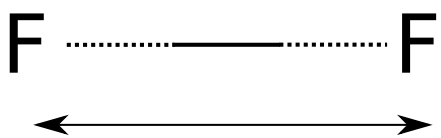
Context

Coupled-Cluster (CC) methods :

- Chemical Accuracy : $\sim$ 1 kcal/mol
- Additivity of energies for splitting on closed shell subsystems
- Can be systematically improved : Infinite basis set extrapolation

Dissociation of F_2:





$$|\Delta E(\mathrm{CCSD}) - \Delta E(\mathrm{FCI})| \sim 25 \text{ kcal/mol}$$

Failure of Single-Reference CC in particular problems :

- Excited states
- Magnetic systems
- Bond breaking
- Avoided crossings
- *etc* . . .

because the *single-reference anzatz* is not relevant.

We propose a *size-extensive*, *state specific* and *internally decontracted* MR-CC method.

Single reference CC is well defined, but there is no standard solution to the MR-CC problem.

Outline

Single Reference CCSD

- $\Psi_{\mathrm{CC}} = \exp(\hat{T})\Psi_{\mathrm{HF}}$
- CCSD :

$$\begin{aligned} \exp(\hat{T}) &= \exp(\hat{T}_1 + \hat{T}_2) \\ &= 1 + (\hat{T}_1 + \hat{T}_2) + 1/2(\hat{T}_1 + \hat{T}_2))^2 + \dots \end{aligned}$$

- In the basis of Slater determinants :

$$|\Psi_{\mathrm{CC}}\rangle = |\mathrm{HF}\rangle + \sum_{I \in \mathrm{FCI}} d_I |I\rangle$$

- The energy can be given by projection on $|\mathrm{HF}\rangle$

$$E_{\mathrm{CC}} = \frac{\langle \mathrm{HF}|\mathcal{H}|\Psi_{\mathrm{CC}}\rangle}{\langle \mathrm{HF}|\Psi_{\mathrm{CC}}\rangle}$$

Single Reference CCSD

$\mathcal{H}$ is a two-body operator $\longrightarrow$ only singles and doubles contribute to the energy by projection on HF

We search for accurate amplitudes only on the single/double excitations

Single Reference CCSD

- CCSD eigenvalue equations : (projection on the Singles/Doubles)

$$\mathcal{H} e^{\hat{T}} |\mathrm{HF}\rangle = E e^{\hat{T}} |\mathrm{HF}\rangle$$
$$\langle i | \mathcal{H} e^{\hat{T}} |\mathrm{HF}\rangle = d_i E$$
$$\langle i | \mathcal{H} |\mathrm{HF}\rangle + \sum_j d_j \langle i | \mathcal{H} | j \rangle + \sum_\alpha d_\alpha \langle i | \mathcal{H} | \alpha \rangle = d_i E$$
$$H_{i0} + d_i (H_{ii} - E) + \sum_{j \neq i} d_j H_{ij} + \sum_\alpha d_\alpha H_{i\alpha} = 0$$

- Exponential parametrization $\longrightarrow$ Amplitudes of the Quadruples are obtained from the amplitudes of the Doubles :

$$d_\alpha = \sum_{(i,j)} d_i d_j \qquad (i,j) : \hat{T}_\alpha = \hat{T}_i \hat{T}_j$$

Dressed Hamiltonian formalism

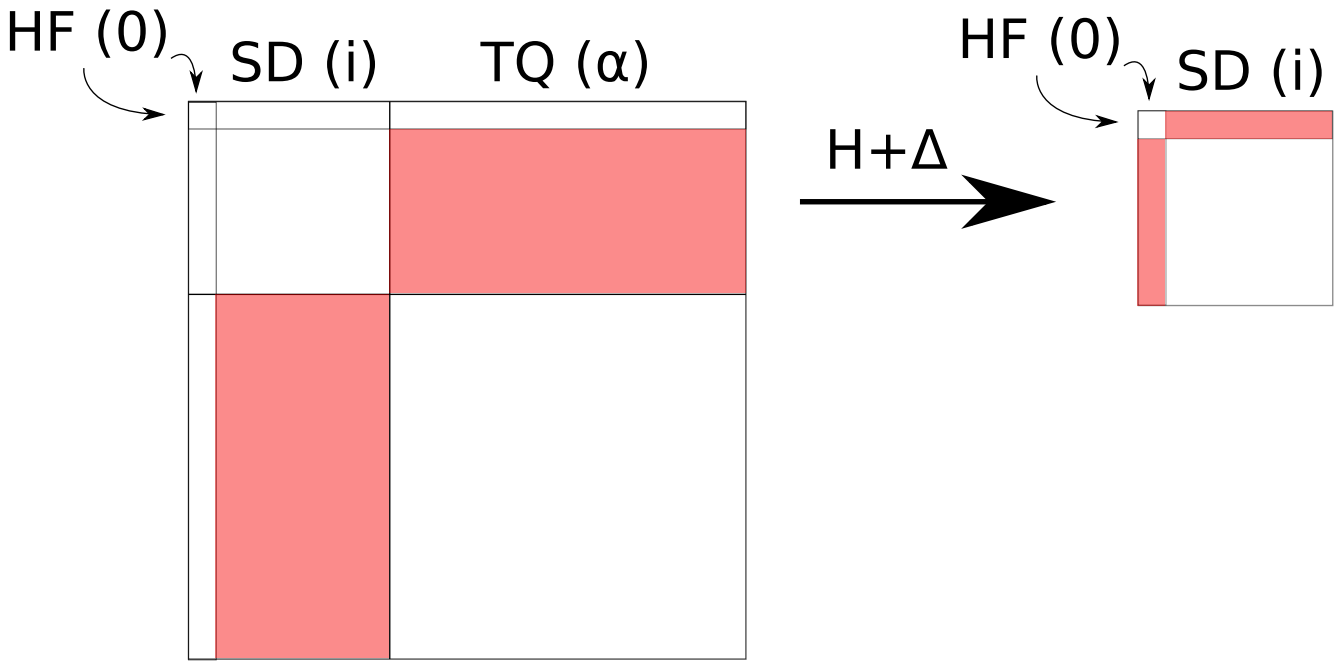
- Start from the CISD : the initial d_i are the c_i/c_0
- Compute the contribution of the Quadruples $|\alpha\rangle$:

$$\sum_{\alpha} d_\alpha H_{i\alpha} = \sum_{(j,k)} d_j d_k H_{jk} \qquad (j,k) : \hat{T}_\alpha = \hat{T}_j \hat{T}_k$$

- Column dressing: $\Delta_{i0} = \sum_\alpha d_\alpha H_{i\alpha}$

$$(H_{i0} + \Delta_{i0}) + d_i(H_{ii} - E) + \sum_{j \neq i} d_j H_{ij} = 0$$

Dressed Hamiltonian formalism



- Diagonalize $H + \Delta$
- Iterate

Outline

Multi-Reference Coupled Cluster

Notations :

- $|I\rangle$: Reference determinants (typically a CAS)
- $|i\rangle$: Singles and Doubles wrt $|I\rangle$ (CAS + SD)
- $|\alpha\rangle$: Triples and Quadruples wrt $|I\rangle$ (CAS + SD + TQ)
- c_i : CI coefficient of determinant i

Multi-Reference Coupled Cluster

Preparation:

- Start with a CAS-SCF:

$$\Psi_{\text{ref}} = \sum_I c_I |I\rangle$$

- Compute all the singles and doubles $|i\rangle$ on top of Ψ_{ref} and diagonalize

$$\Psi_{\text{CAS+SD}} = \sum_I c_I |I\rangle + \sum_i c_i |i\rangle$$

- We can rewrite $c_i = \sum_I c_I d_{Ii}$

$$\Psi_{\text{CAS+SD}} = \sum_I c_I \left(|I\rangle + \sum_i d_{Ii} |i\rangle \right)$$

Multi-Reference Coupled Cluster

$$\Psi_{\text{CAS+SD}} = \sum_I c_I \left(|I\rangle + \sum_i d_{Ii} |i\rangle \right)$$

$|i\rangle$ appears in the expansion of multiple $|I\rangle$: "multi-parentage problem"

- How much of c_i do we give to each $|I\rangle$?
- How do we determine the d_{Ii}?

Perturbative estimation:

$$c_i = \sum_I \frac{\langle \Psi_{\text{CAS}} | \mathcal{H} | i \rangle}{E - \langle i | \mathcal{H} | i \rangle} = \sum_I c_I \frac{\langle I | \mathcal{H} | i \rangle}{E - \langle i | \mathcal{H} | i \rangle} = \sum_I c_I d_{Ii}$$

The ratio of the amplitudes does not depend on the reference wave function:

$$\frac{d_{Ii}}{d_{Ji}} = \frac{\langle I | \mathcal{H} | i \rangle}{\langle J | \mathcal{H} | i \rangle}$$

Multi-reference Anzatz[1]

We impose:

$$\frac{d_{Ii}}{d_{Ji}} = \frac{\langle I|\mathcal{H}|i\rangle}{\langle J|\mathcal{H}|i\rangle}$$

[1] J. Meller, J. P. Malrieu, R. Caballol, *J. Chem. Phys.* **104**, 4068 (1996)

Multi-Reference Coupled Cluster

- Generate quadruple excitations $|\alpha\rangle$ with respect to $|I\rangle$:

$$\begin{aligned}\Psi &= \sum_I c_I|I\rangle + \sum_i c_i|i\rangle + \sum_\alpha c_\alpha|\alpha\rangle \\ &= \sum_I c_I \left(|I\rangle + \sum_i d_{Ii}|i\rangle + \sum_\alpha d_{I\alpha}|\alpha\rangle \right)\end{aligned}$$

- "Coupled-Clusterize" with respect to each $|I\rangle$:
  Impose $d_{I\alpha}$ such that

$$d_{I\alpha} = \sum_{(i,j)} d_{Ii} d_{Ij} \quad , \quad \{(i,j)|\hat{T}_\alpha = \hat{T}_i \hat{T}_j\}$$

Eigenvalue equations

Eigenvalue equation for $|i\rangle$:

$$\langle i|H|\Psi\rangle = E\langle i|\Psi\rangle$$

$$c_i H_{ii} + \sum_I c_I H_{Ii} + \sum_j c_j H_{ij} + \sum_\alpha c_\alpha H_{i\alpha} = E c_i$$

$$c_i (H_{ii} - E) + \sum_I c_I H_{Ii} + \sum_j c_j H_{ij} + \sum_\alpha c_\alpha H_{i\alpha} = 0$$

Inserting the amplitudes :

$$c_i (H_{ii} - E) + \sum_I c_I \left(H_{Ii} + \sum_j d_{Ij} H_{ij} + \sum_\alpha d_{I\alpha} H_{i\alpha} \right) = 0$$

Dressed Hamiltonian formalism

$$c_i(H_{ii} - E) + \sum_I c_I \left(H_{Ii} + \sum_j d_{Ij} H_{ij} + \sum_\alpha d_{I\alpha} H_{i\alpha} \right) = 0$$

Define a *dressing* term Δ_{Ii} between $|I\rangle$ and $|i\rangle$:

$$\Delta_{Ii} = \sum_\alpha d_{I\alpha} H_{i\alpha}$$

The eigenvalue equation becomes:

$$c_i(H_{ii} - E) + \sum_I c_I \left(H_{Ii} + \sum_j d_{Ij} H_{ij} + \Delta_{Ii} \right) = 0$$

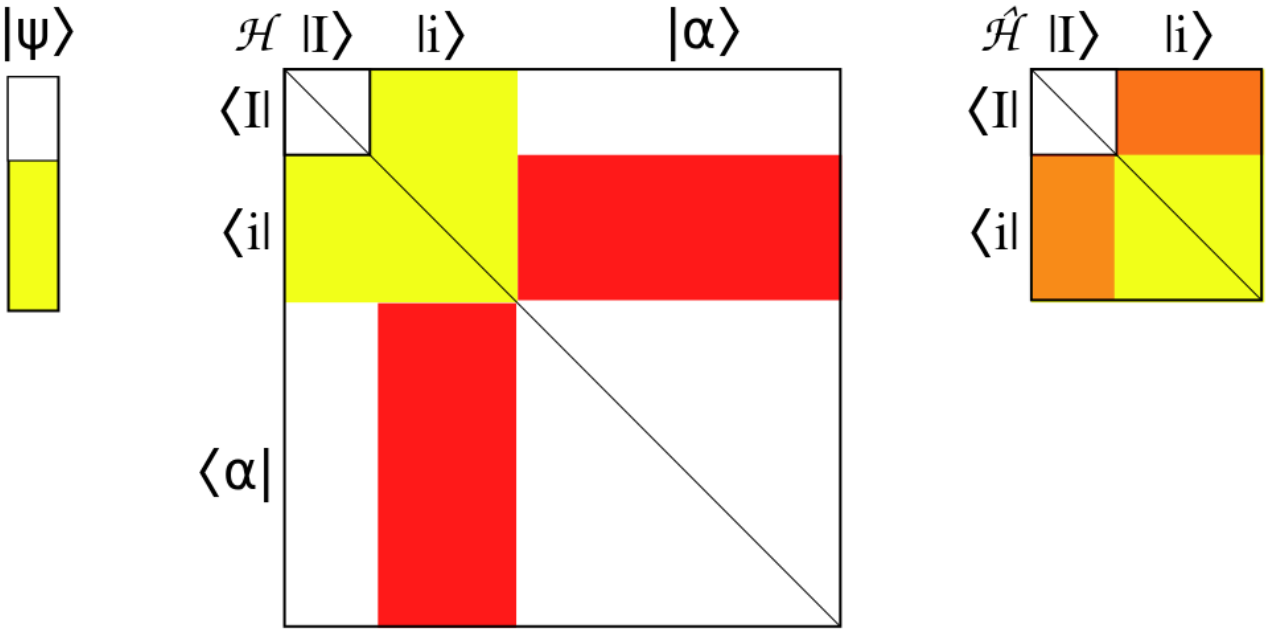
Back to the CI representation :

$$c_i(H_{ii} - E) + \sum_I c_I (H_{Ii} + \Delta_{Ii}) + \sum_j c_j H_{ij} = 0$$

Dressed Hamiltonian formalism

$$c_i(H_{ii} - E) + \sum_I c_I(H_{Ii} + \Delta_{Ii}) + \sum_j c_j H_{ij} = 0$$

This is the eigenvalue equation of a modified Hamiltonian including the effect of the triples/quadruples:



Dressed Hamiltonian formalism

- Diagonalize the dressed Hamiltonian
- Iterate until the eigenvalue converges

Outline

Implementation

Quantum Package : Library for programming post-HF methods with *no effort*.[2]
Efficient determinant-driven calculations[3]:

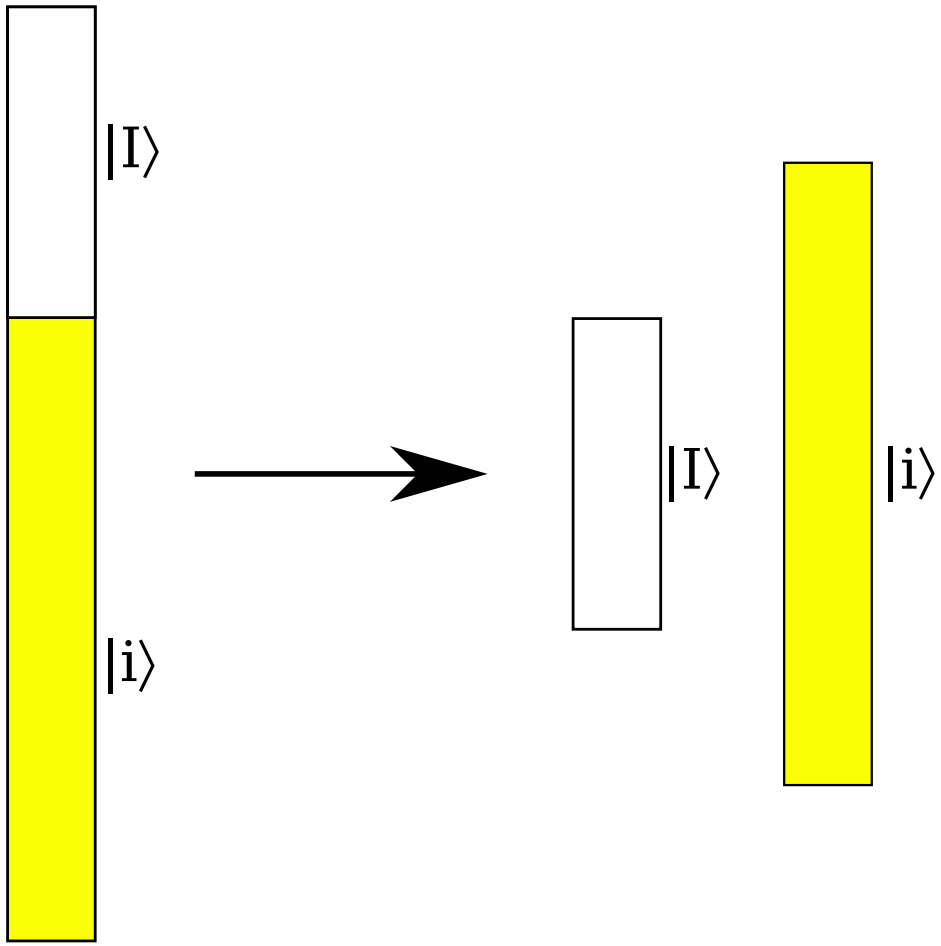
- Excitation degree between $|i\rangle$ and $|j\rangle$: 10 CPU cycles (faster than FP division)
- Single excitation operator : 50 CPU cycles
- Double excitation operator : 80 CPU cycles

Our MR-CC algorithm relies on determinant comparisons

[2] `https://github.com/LCPQ/quantum_package`
[3] A.S., E. Giner, arXiv:1311.6244 [physics.comp-ph]

Implementation

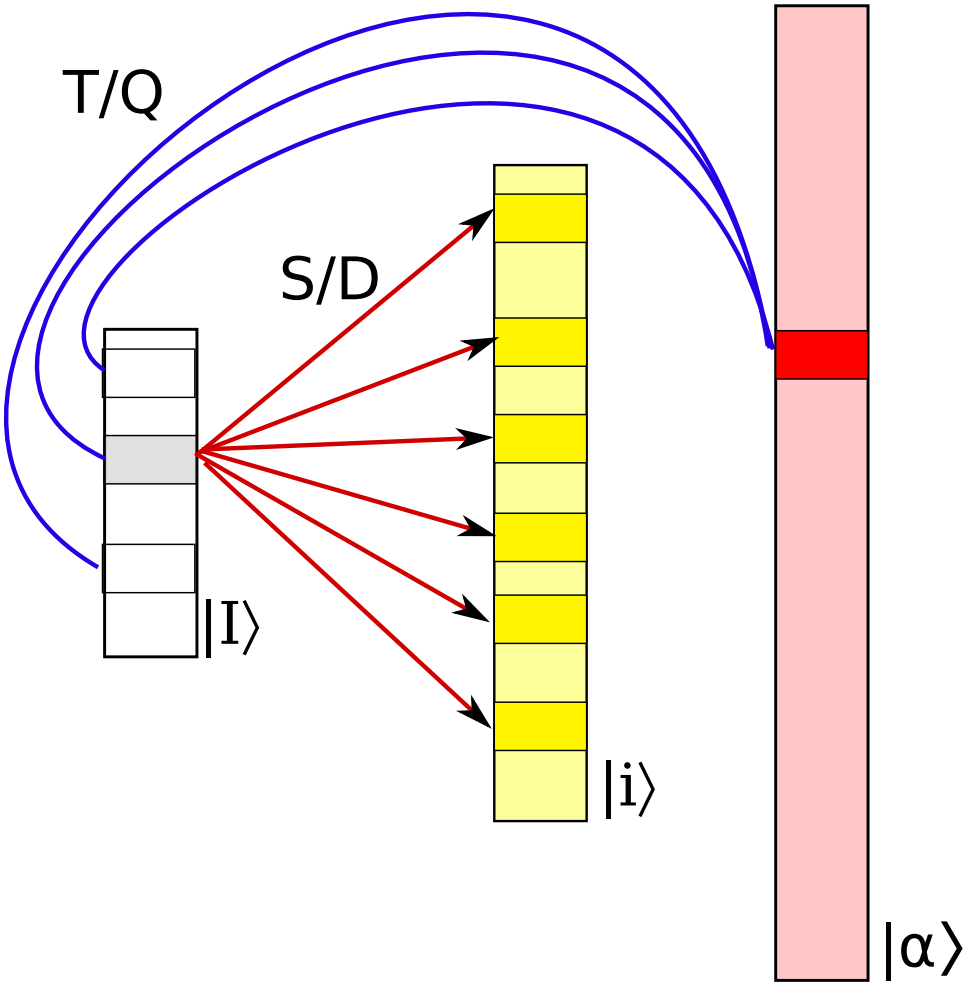
- Split the CAS+SD wave function in CAS and SD :



Implementation

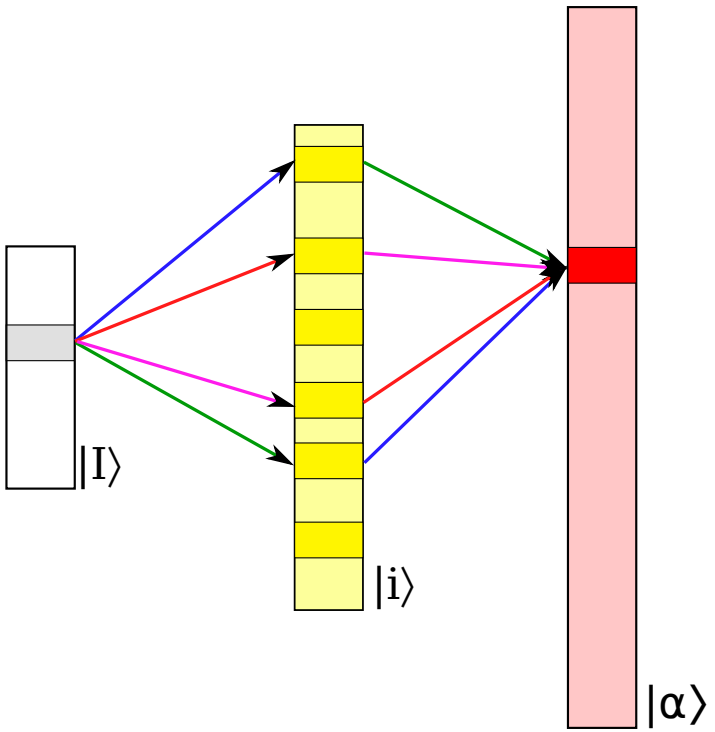
- Generate all possible Singles and Doubles from $|i\rangle$
- The $|\alpha\rangle$ are those which are not already in $\Psi_{\mathrm{CAS+SD}}$
- For each $|\alpha\rangle$:
  - Get the excitation degree from all $|I\rangle \rightarrow |\alpha\rangle$
  - Degrees 3 and 4 : *grand-parents* of $|\alpha\rangle$
  - Get the excitation degree from all $|I\rangle \rightarrow |i\rangle$
  - Degrees 2 and 1 : *parents* of $|\alpha\rangle$ between $|I\rangle$ and $|\alpha\rangle$

Implementation



Implementation

- Compute $d_{I\alpha} = \sum_{(i,j)} d_{Ii} d_{Ij}$
  - For each selected $|i\rangle$, find operators $\hat{T}_{I\to i}$ and $\hat{T}_{i\to\alpha}$
  - Apply $\hat{T}_{i\to\alpha}$ on $|I\rangle$ to get $|j\rangle$
  - Fetch the corresponding d_j

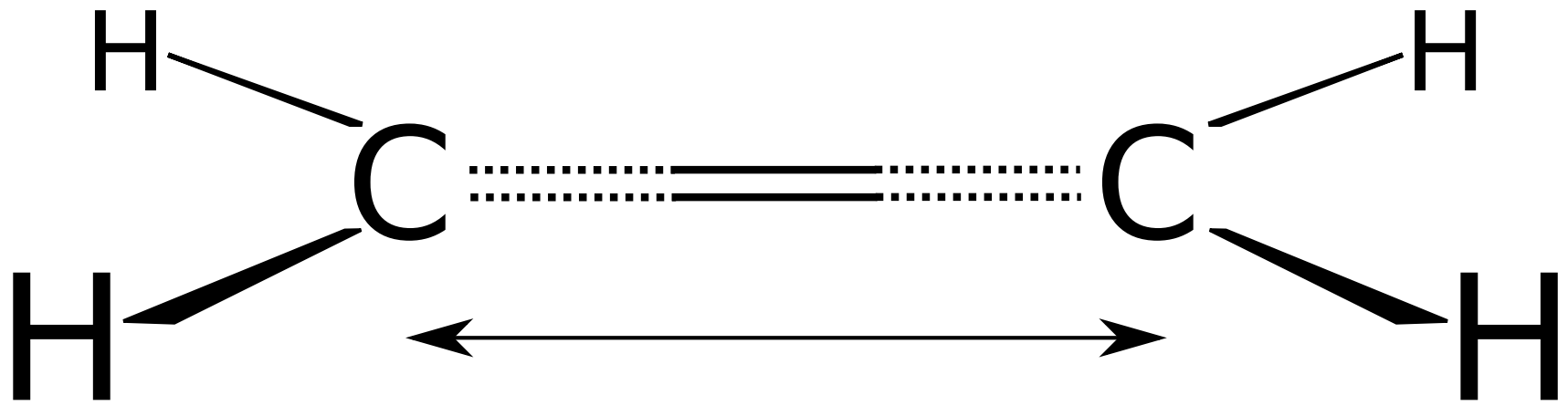


Implementation

- Add the contribution $d_{I\alpha}H_{\alpha i}$ to all columns i of Δ_{Ii}
- Symmetrize Δ
- Add Δ to $\mathcal{H}$
- Get the lowest eigenpair of $\mathcal{H}$ (Davidson)
- Iterate

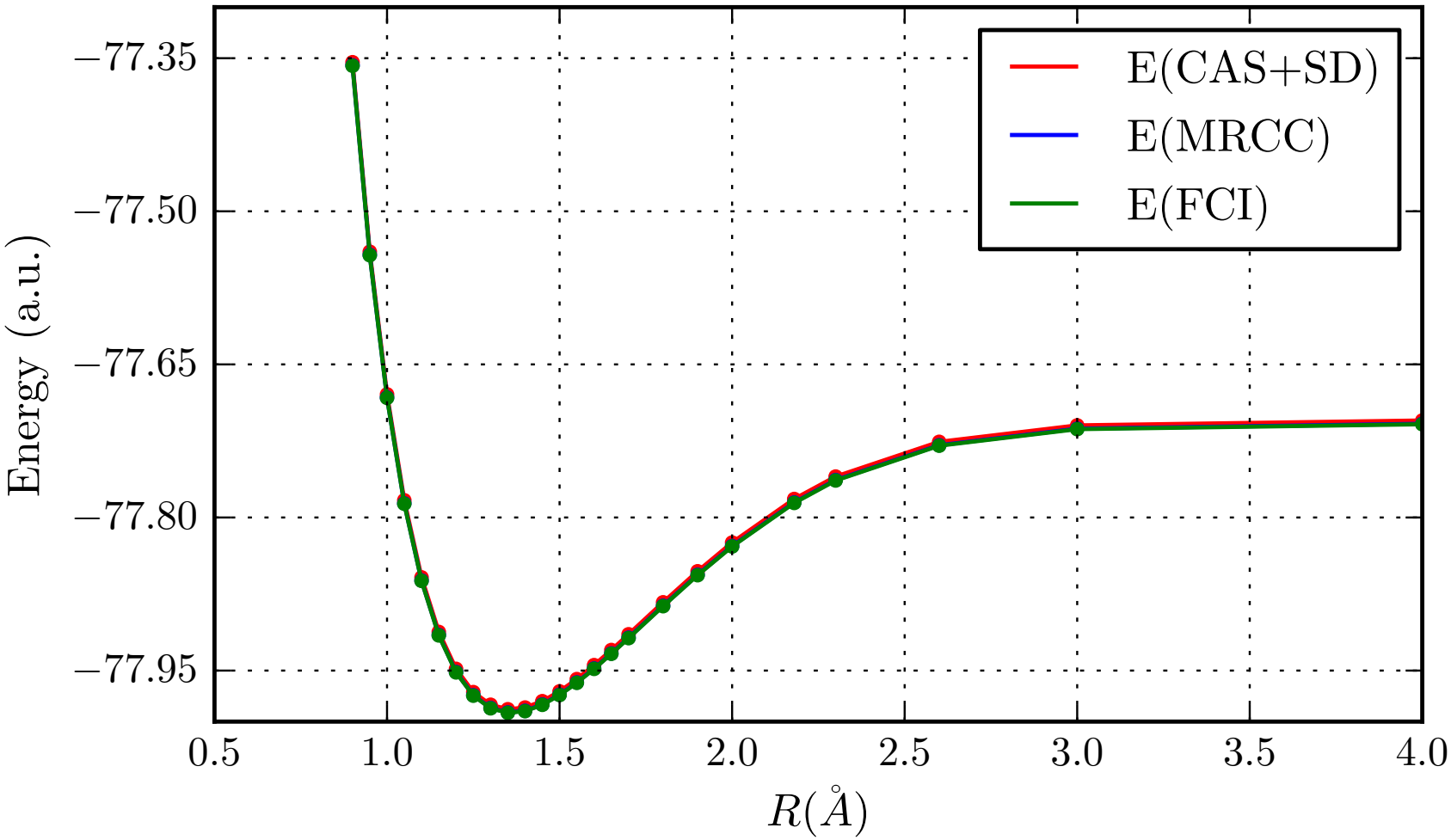
Outline

Stretching of C_2H_4

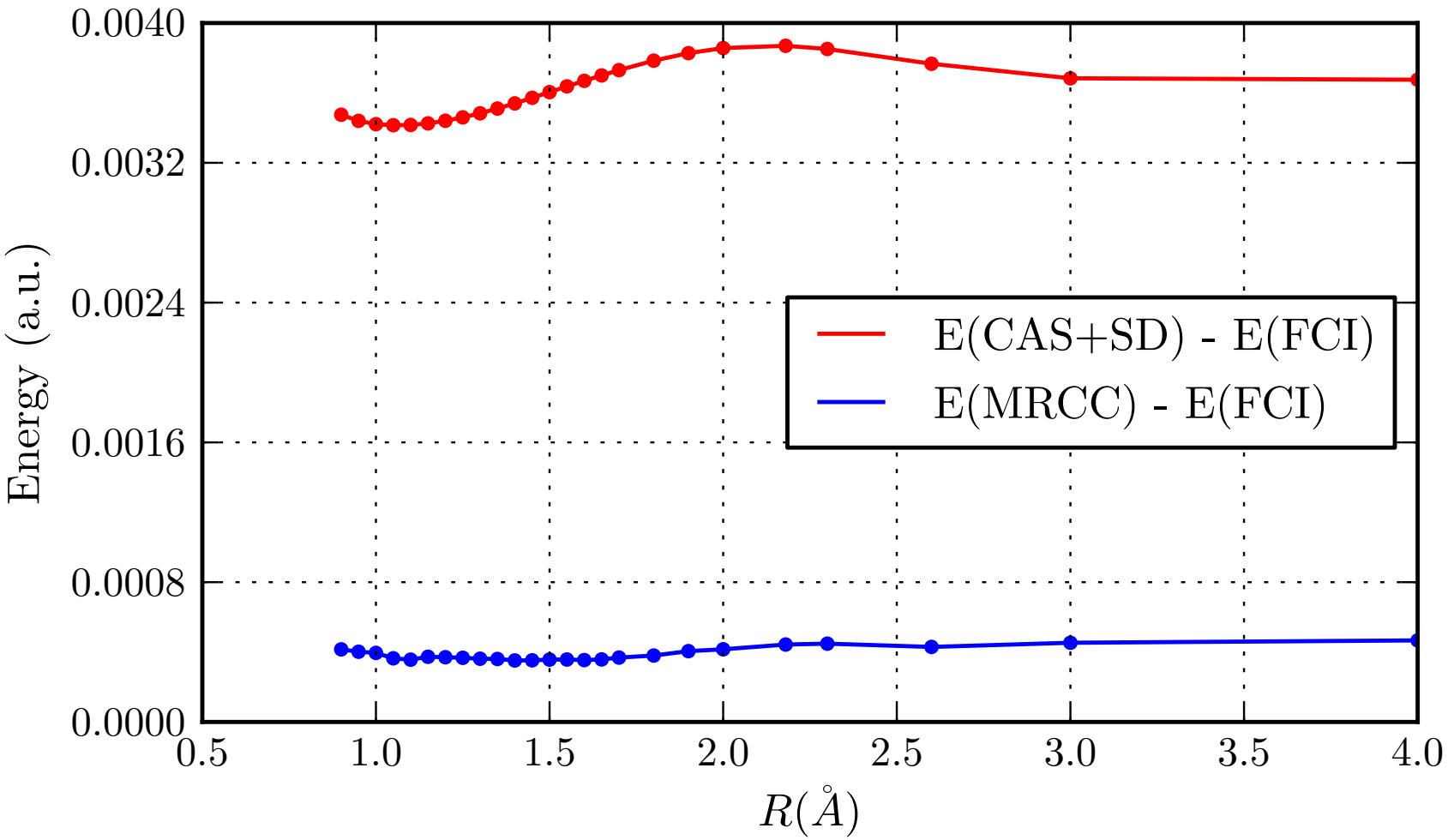


CAS: 4 electrons in 4 MOs

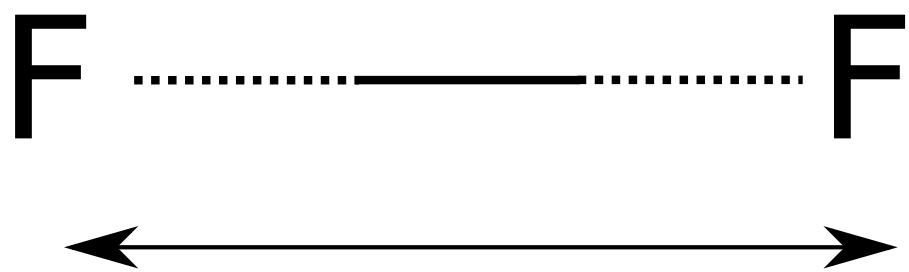
Stretching of C_2H_4



Stretching of C_2H_4

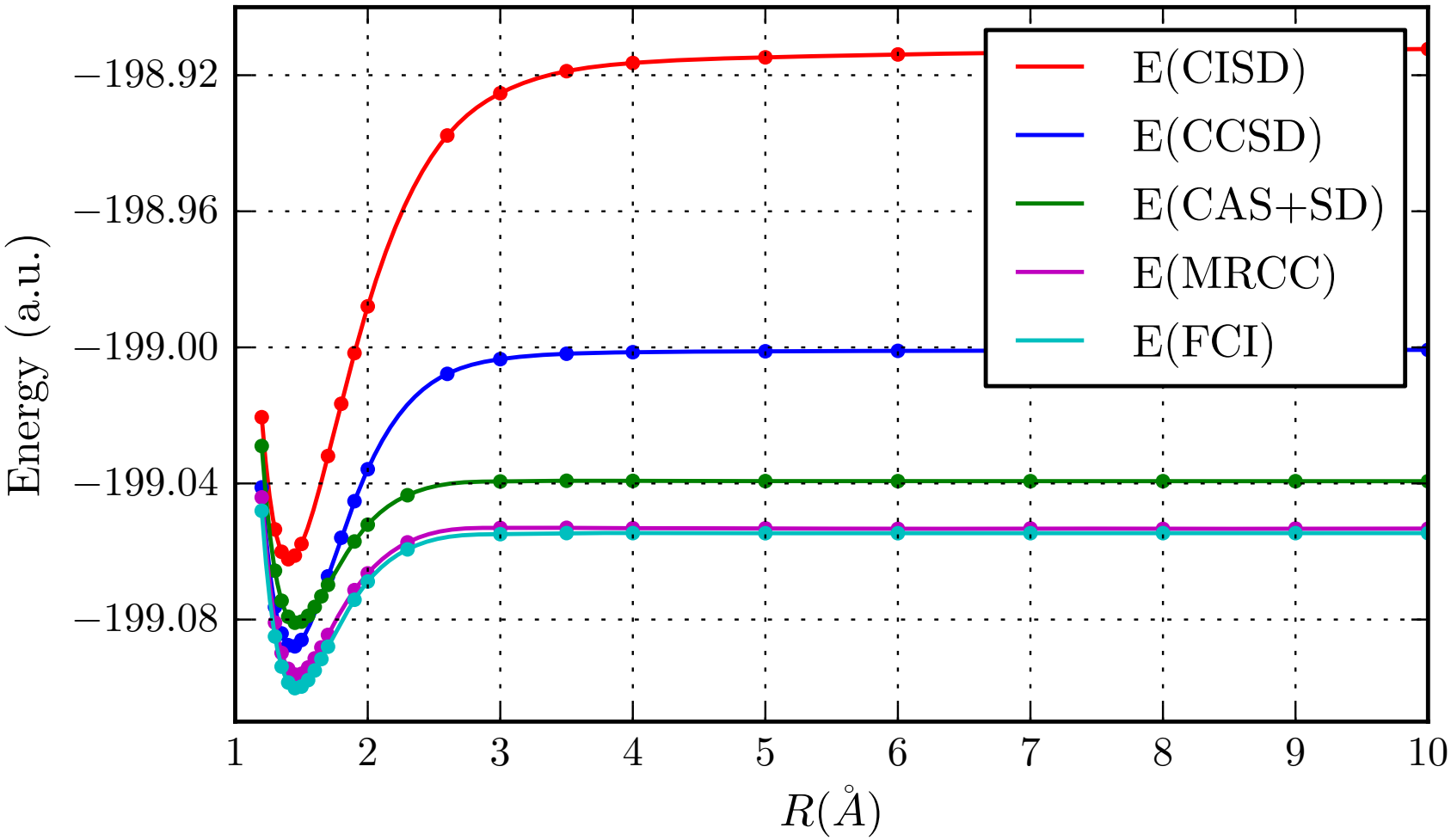


Breaking of F_2

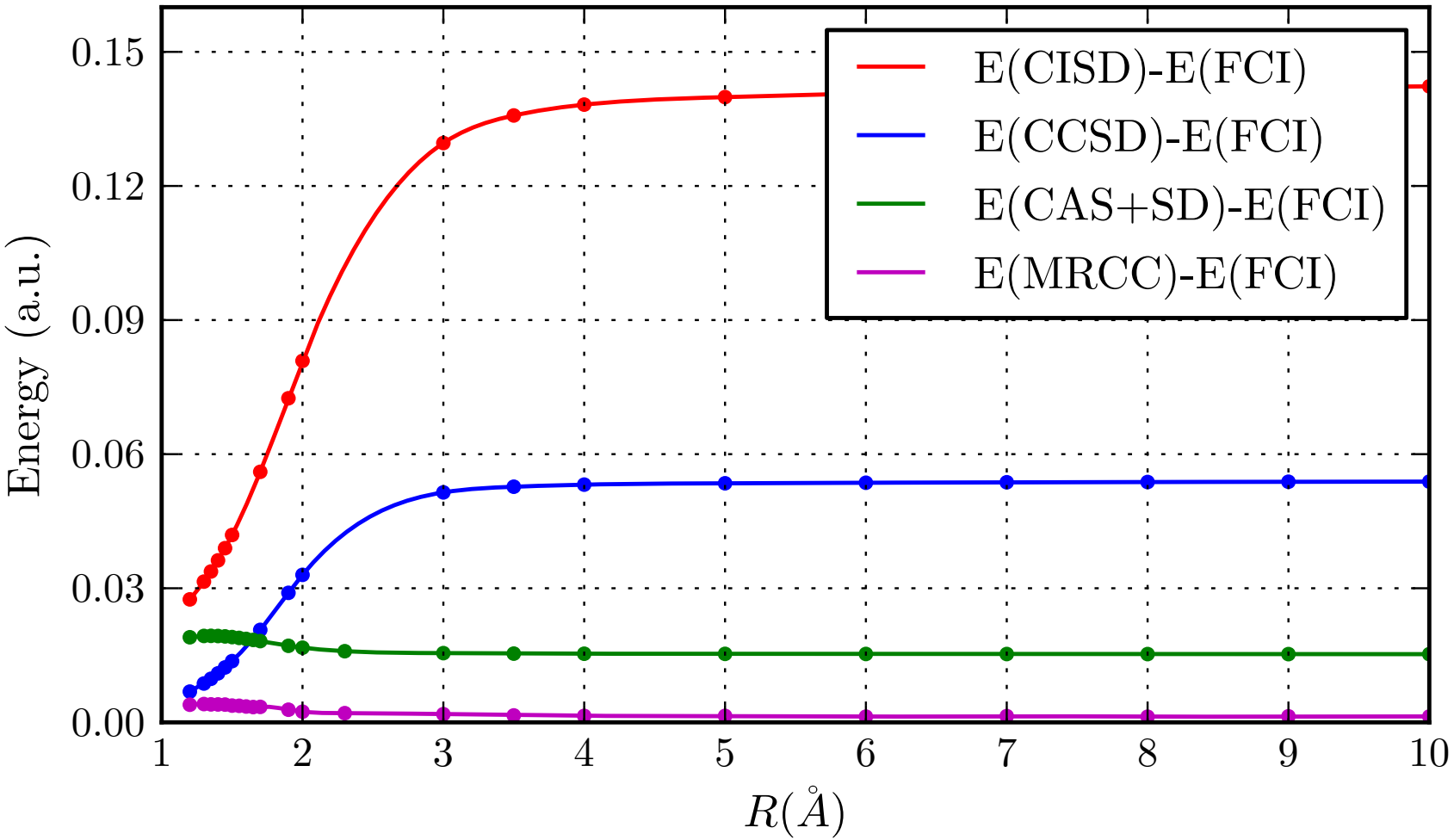


CAS: 2 electrons in 2 MOs

Breaking of F_2



Breaking of F_2



Breaking of F_2

Average error $\langle E - E(FCI) \rangle$

	min (mEh)	max (mEh)	max - min (kcal/mol)
CISD	27.5	142.3	72.04
CCSD	6.9	53.8	29.43
CAS+SD	15.3	19.3	2.51
MR-CCSD	1.3	4.1	1.76

cc-pVDZ basis set